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KINETIC STUDIES ON FAST REACTIONS IN SOLUTION

II The Reaction between 1, 3, 5-Trinitrobenzene and Diethylamine in Acetone

BY JIRO OSUGI AND MUNEO SASAKI

The reaction between 1, 3, 5-trinitrobenzene (TNB) and diethylamine (DEA) in acetone was investigated at room temperature by the stopped flow method.

By measuring the optical densities at 472 and 516 $m\mu$ in the course of the reaction, it was found that the reaction proceeded in two consecutive steps; one is moderately fast and the other is slow. The stoichiometry of the intermediate having a maximum peak at 470 $m\mu$ may be one TNB molecule and one DEA molecule. This reaction is reversible and of first order both in TNB and in DEA.

The influence of "aging" of DEA in acetone is conspicuous on the rate of increase in the optical density at 516 $m\mu$. It was indicated from an elementary analysis and an infrared spectrum of the product that the product-complex having the maximum peak at 520 $m\mu$ may possess the stoichiometry, 1 : 2 : 1, for TNB, DEA and acetone. The overall reaction was discussed from the view point of kinetics.

Introduction

It has been found that aromatic poly-nitrocompounds react with aromatic amines to form charge-transfer (C-T) complexes¹⁾. For the reactions with aliphatic amines, however, there has been no evidence whether the products are C-T complexes^{2)~4)} or Meisenheimer complexes^{5)~7)}. On the reactions between poly-nitrocompounds and aliphatic amines, in general, slow reactions proceed following an initial fast reaction^{4)~8)}.

The nucleophilic substitution reactions of aromatic poly-nitrocompounds with OH^- , EtO^- or MeO^- proceed through the purple Meisenheimer complex^{9)~12)}; and these reactions were studied from the view point of kinetics^{13)~16)}.

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For aliphatic amines, the stoichiometry of the complexes and thermodynamic parameters in equilibria were investigated²⁾⁶⁾⁷⁾⁹⁾, but the authors can find no kinetic study, except that of Caldin and his co-workers made at low temperature. On this paper the reaction of TNB with DEA in acetone solution was studied kinetically, the properties of the complexes and the overall reaction scheme being considered at room temperature. The authors, however, have obtained the quite different results from those of Caldin. In this case, a series of reaction may be undergone, and an initial fast reaction was followed by a slow reaction on which a significant influence of "aging" of DEA in acetone was found. Moreover, NMR studies by Foster *et al.*, have confirmed the addition of conjugated base of acetone to TNB in the same system⁸⁾.

The reaction rates were pursued by the stopped flow method⁴⁾¹⁷⁾ observing optical densities at 472 and 516 m μ .

Experimentals

Materials

1, 3, 5-trinitrobenzene was recrystallized three times from ethanol (mp 123°C). Diethylamine was distilled from solid potassium hydroxide and redistilled in vacuum just before each run (bp 55.5°C).

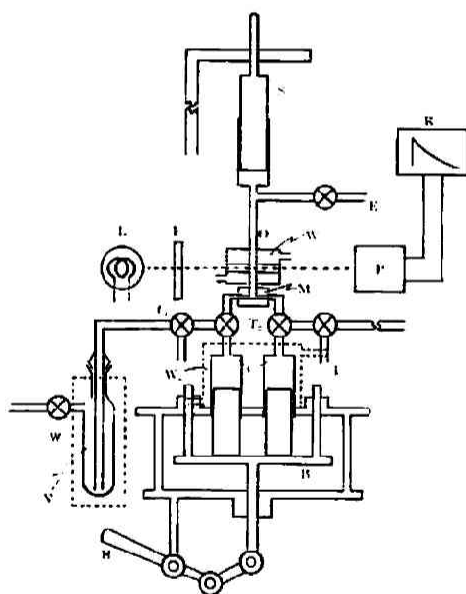


Fig. 1 Schematic diagram of flow apparatus

- B: Pushing board
- C: Hypodermic syringes
- E: Outlet of reacting solution
- F: Interference filter
- H: Handle
- I: Inlet of liquid for washing
- L: Monitoring lamp
- M: Mixing chamber
- O: Observation tube
- P: Photomultiplier
- R: Oscilloscope or recorder
- S: Stopper
- V: Reservoir of reacting solution
- W₁, W₂, W₃: Thermostat and water jackets
- T₁, T₂: Three-way taps

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- 15) (a) E. F. Caldin and J. C. Trickett, *ibid.*, 49, 772 (1953)
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The solvent was acetone which was dried with potassium carbonate and distilled, having bp 56.5°C.

Apparatus

The general construction was drawn in Fig. 1. The mixing chamber (M) was made of teflon and both reacting solutions were led through glass tubes (2 mm ϕ). Four jets delivered tangentially. A glass tube was used for an observation tube and the position of observation was 15 mm from the position of mixing.

Method of fluid drive

In Fig. 1, (V) is the reservoir of a reacting solution, (C) are glass hypodermic syringes, (I) being the inlets of liquid to wash the system. The reacting solutions, being led into (C) by operating three-way taps (T_1), (T_2), and the handle (H), can be driven tangentially into the mixing chamber by pushing the board (B) upward. Although the flow velocity was not constant over all runs*¹ because of the manual operation of fluid drive, the mixing time at 10 ml/sec of velocity was less than 10 msec by means of dilution. A hypodermic syringe was used for the stopper (S), and (E) is an outlet of the solution after each run.

Measurement

The filters to obtain required monochromes, a photomultiplier and an oscillograph or a recorder were aligned. The response time was less than 1 msec.

Procedure

The acetone solutions of TNB and DEA were reserved in (V) at constant temperature. The reacting solutions, led into (C), were driven into the mixing chamber; this operation was repeated several times*². The board (B) was pushed upward, and just after the flow stopped the optical density was recorded on an oscillograph or on a recorder. It should be noticed that the concentrations of both reactants in the observation tube are one half of those in the reservoirs.

Results

The absorption spectrum of TNB and DEA shows two peaks at 470 and 520 m μ immediately after mixing, the intensities of which develop slowly with time, and after long time (about 3 hours) the mixture has only one peak at 520 m μ . TNB in DEA solution (without acetone) shows only a broad absorption band between 400~500 m μ , but the addition of a large quantity of acetone modified the

* 1 Unless the fluctuation of mixing time is important, it is not necessary to know accurate flow velocity in the stopped flow method. In this work the half lives of the reactions are longer than 0.1 sec, so the fluctuation of the mixing time at each run can be negligible so far as the variation of flow velocity is not so serious.

* 2 This operation was performed to fill the observation tube with the solutions.

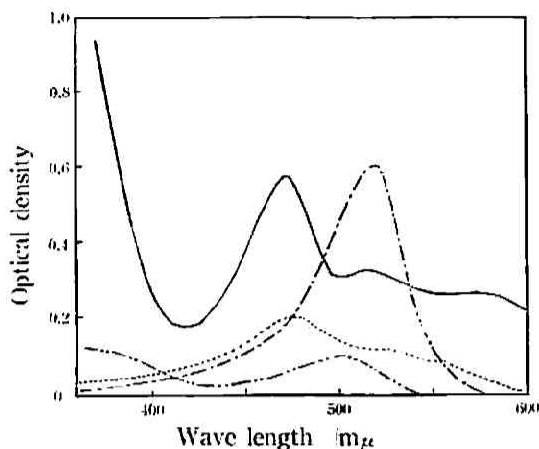


Fig. 2 Visible absorption spectra of TNB-DEA in acetone

$[\text{TNB}]_0 = 1.4 \times 10^{-5}$ mole/l

$[\text{DEA}]_0 = 1.0 \times 10^{-2}$ mole/l

-----: immediately after mixing

- - - - -: 3 hours after mixing

- · - · - : HCl aqueous solution was added

—: $[\text{TNB}]_0 = 1.0 \times 10^{-2}$ mole/l

$[\text{DEA}]_0 = 9.5 \times 10^{-5}$ mole/l

spectrum into that quite similar to the broken curve (— · —) in Fig. 2. Reddish dark precipitate has been obtained by addition of ether immediately after the dissolution of TNB (0.1 g) and DEA (1 ml) into acetone (5 ml), which shows two peaks, strong at 470 mμ and weak at 560 mμ, (10:1), in ethanol. But in acetone with DEA added, its spectrum approaches slowly to that similar to the broken curve (— · —) in Fig. 2.

Foster recognized that the reaction, $(\text{TNB} - \text{NEt}_2)^- \longrightarrow (\text{TNB} - \text{CH}_2\text{COCH}_3)^-$, proceeds in acetone and that $(\text{TNB} - \text{CH}_2\text{COCH}_3)^-$ has two peaks at 464 and 555 mμ in methanol (2.3:1)¹⁸⁾. This step is slow, and so the development of optical density at 472 mμ in the present case, which is fast, is attributable to the reaction between TNB and DEA.

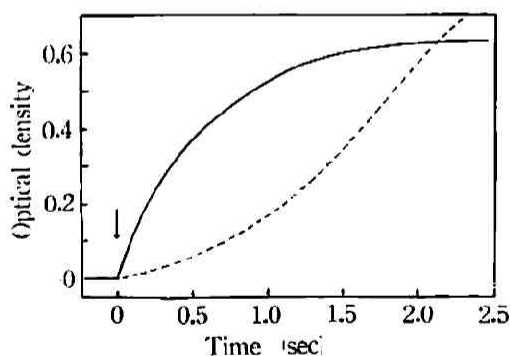


Fig. 3 Typical oscillograph traces at 472 mμ and 516 mμ. The arrow shows the point of flow-stopping.

$[\text{TNB}]_0 = 3.0 \times 10^{-4}$ mole/l

$[\text{DEA}]_0 = 8.9 \times 10^{-2}$ mole/l

— 472 mμ

- - - 516 mμ

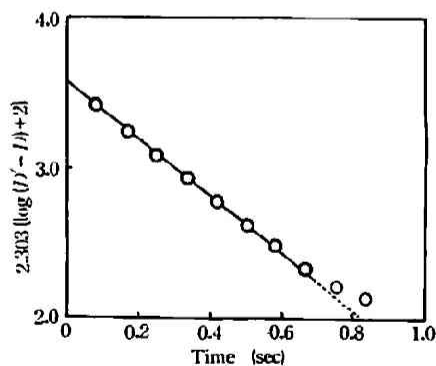


Fig. 4 Guggenheim's plot at 472 mμ

$[\text{TNB}]_0 = 3.0 \times 10^{-4}$ mole/l

$[\text{DEA}]_0 = 8.9 \times 10^{-2}$ mole/l

18) R. Foster and C. A. Fyfe, *J. Chem. Soc.*, 1966 B, 53

The development of optical density at $516\text{m}\mu$ with time was seriously dependent on "aging time"^{*3}, as will be described later, although that at $472\text{m}\mu$ was not. The traces shown in Figs. 3 and 6 were analyzed for the initial fast and the following slow reactions, respectively.

Fast reaction (the measurement at $472\text{m}\mu$)

Runs were carried out in acetone in the range of $(1.5\sim 3.0)\times 10^{-4}$ mole/l for TNB and $(2.13\sim 11.55)\times 10^{-2}$ mole/l for DEA. The first order plots prepared by Guggenheim's method¹⁹⁾ were almost always linear within experimental error in the initial region of the trace in Fig. 3. The numerical value of the slope is denoted by S , the plots of which against $[\text{DEA}]_0$ give straight lines (Fig. 5).

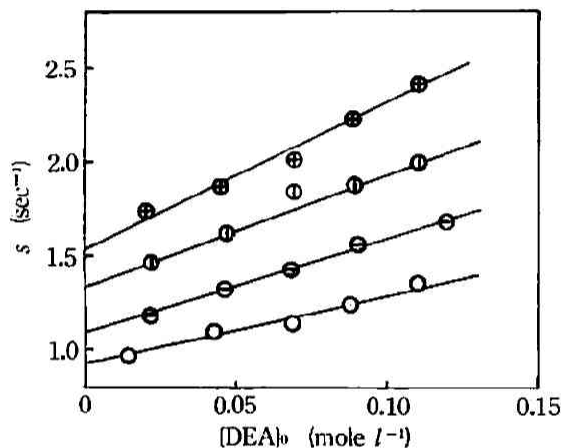


Fig. 5 Plots of slopes S vs. $[\text{DEA}]_0$

—○—○— : 15°C
 —○—○— : 20°C
 —○—○— : 25°C
 —○—○— : 30°C

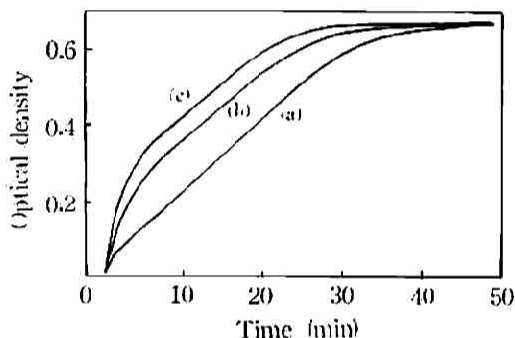


Fig. 6 Change of optical density with time and influence of aging
 $[\text{TNB}]_0 = 1.15 \times 10^{-4}$ mole/l, $[\text{DEA}]_0 = 2.97 \times 10^{-2}$ mole/l
 Aging time (min);
 a : 7 b : 52 c : 120

$$S = k_f[\text{DEA}]_0 + k_b \quad (1)$$

This linear S - $[\text{DEA}]_0$ relationship is characteristic of a reversible reaction of the type, $\text{A} + \text{B} \rightleftharpoons \text{C}$, where either A or B is in much excess⁴⁾. k_f and k_b were obtained from the slopes and intercepts of Fig. 5, the energies of activation (E) and entropies of activation (ΔS^\ddagger) being obtained for the forward and back reactions; furthermore the equilibrium constant and corresponding thermodynamic parameters, ΔH° and ΔS° were calculated from the following relations and all these numerical values are given in Table 1.

$$\left. \begin{aligned} K &= \frac{k_f}{k_b} \\ \Delta H^\circ &= E_f - E_b \\ \Delta S^\circ &= \Delta S_f^\ddagger - \Delta S_b^\ddagger \end{aligned} \right\} \quad (2)$$

* 3 The time interval from the preparation of both reacting solutions until the mixing in the mixing chamber.

19) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926)

Table 1 Kinetic and thermodynamic parameters

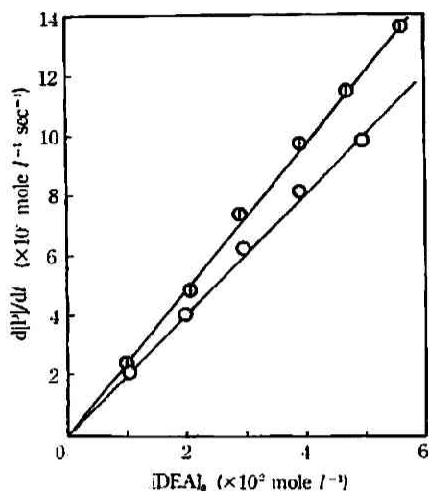
Temperature (°C)	15	20	25	30
k_f (l mole ⁻¹ sec ⁻¹)	3.55	4.75	5.80	7.60
k_b (sec ⁻¹)	0.94	1.11	1.34	1.55
K (l mole ⁻¹)	3.72	4.28	4.33	4.90
E_f (kcal mole ⁻¹)		8.70		
E_b (kcal mole ⁻¹)		5.2		
ΔS_f^\ddagger (cal mole ⁻¹ deg ⁻¹)		-27.8		
ΔS_b^\ddagger (cal mole ⁻¹ deg ⁻¹)		-42.6		
ΔH^\ddagger (kcal mole ⁻¹)		3.5		
ΔS^\ddagger (cal mole ⁻¹ deg ⁻¹)		14.8		

Table 2 The slopes of linear changes of optical density at 516 m μ

Temperature (°C)	[TNB] ₀ × 10 ⁴ mole l ⁻¹	[DEA] ₀ × 10 ² mole l ⁻¹	aging time (min)	slope × 10 ⁴ mole l ⁻¹ sec ⁻¹
25	1.55	1.00	8	2.20
	1.15	1.03	48	2.20
	1.15	1.03	121	2.27
	1.15	1.03	184	2.26
	1.15	2.02	6	4.08
	1.15	2.02	53	3.78
	1.15	2.02	123	4.06
	1.15	2.97	7	6.18
	1.15	2.97	52	6.84
	1.15	2.97	120	6.36
	1.15	3.89	8	8.12
	1.15	3.89	30	9.12
	1.15	3.89	60	9.82
	1.15	4.85	5	9.63
	1.15	4.85	60	9.61
	1.15	4.85	72	9.61
	1.15	1.01	5	2.07
	1.22	2.07	7	4.71
30	1.22	2.07	55	4.78
	1.22	2.07	97	4.74
	1.15	2.96	6	7.14
	1.15	2.96	29	7.14
	1.15	2.96	94	7.33
	1.00	3.95	5	9.93
	1.00	3.95	39	9.72
	1.00	3.95	67	9.81
	0.90	4.65	5	11.2
	0.80	5.02	5	13.7
	0.80	5.02	33	13.5

Slow reaction (the measurement at 516 m μ)

Fig. 6 shows the changes of optical density at 516 m μ with time, where the influence of aging time is significant in the beginning of the reaction. But after a few minutes, increases of optical density are almost always linear and the slopes of this region are independent of aging time. The numerical values of these slopes are given in Table 2, the plot of which against [DEA]₀ is linear passing through

Fig. 7 Dependence of linear slope on $[\text{DEA}]_0$

—○—○—: 25°C

—⊙—⊙—: 30°C

the origin as illustrated in Fig. 7.

The reaction scheme should be inferred, first of all, from the identification of the reaction product, but unfortunately, in this case, the attempts to determine the products from electronic, infrared and NMR spectra failed. The infrared spectrum of the product after complete dryness in vacuum indicated the existence of $\text{C}=\text{O}$ at 1710 cm^{-1} , NO_2 at $1550\sim 1560\text{ cm}^{-1}$ and the broad absorption between $1000\sim 1300\text{ cm}^{-1}$ which reduced by the addition of acid. However the facts that the anti-symmetrical stretching frequency of NO_2 does not shift from the parent TNB and that $\text{C}=\text{O}$ group remains even after the addition of acid would reject the conclusion that the product is Meisenheimer type¹⁷⁾²⁰⁾²¹⁾.

An elementary analysis also implied the participation of one acetone molecule in the product, that is, the observed stoichiometry of the product is in good agreement with that calculated as 1 : 2 : 1 for TNB, DEA and acetone.

Table 3 Elementary analysis of the product

	C	H	N	O
observed (%)	48.4	7.1	16.6	27.9
†calculated (%)	48.9	7.4	16.7	27.0

† These were calculated assuming 1 : 2 : 1 for TNB, DEA and acetone.

Moreover, the ultra-violet spectrum of DEA in acetone shows the appearance of new peaks, though weak, at 300 and $240\sim 250\text{ m}\mu$, at which the optical densities develop with time.

On the other hand, the influence of aging time on the increase at $472\text{ m}\mu$ was not found; that is because $[\text{TNB}]$ is at least 100 times less than $[\text{DEA}]$ and so the complex, DA, produced from DEA and acetone during the aging is so small that the real concentration of DEA at the mixing does not so much

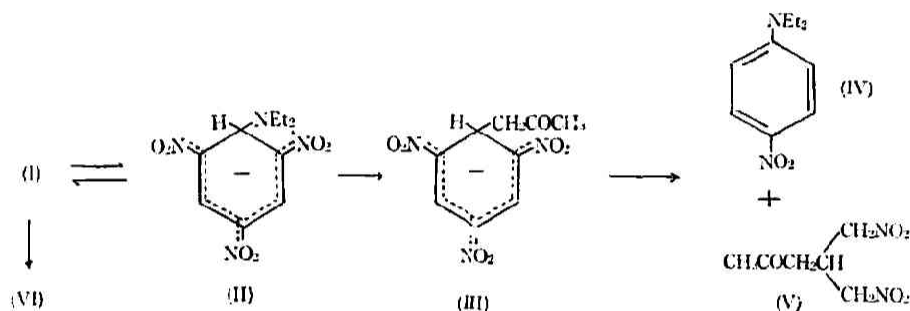
20) L. K. Dyal, *J. Chem. Soc.*, 1960, 5160

21) S. Nagakura, *Tetrahedron Suppl.*, 9, 361 (1963)

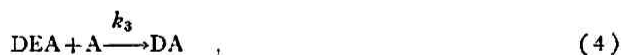
deviate from that at the preparation.

Discussion

The reaction between TNB and aliphatic amines is conspicuously dependent on solvents^{2,3,7}. Caldin investigated the initial fast reaction between TNB and DEA in acetone-water and in acetone-ether at low temperature ($-28.98 \sim -85.60^\circ\text{C}$) from the view point of kinetics⁴. Foster pursued the following slow steps by means of NMR at room temperature and postulated the following reaction scheme⁸.



where (VI) is an unknown substance. Caldin suggested from the rate study that C-T complex (I) is formed from the hydrogen-bonded dimer $(\text{DEA})_2$ and TNB⁴. The present study, however, shows that the rate of formation of the initial complex is of first order with respect to DEA and so the complex, C, is different from (I). The following slow reaction can be regarded as that between the complex and DA; this step will be considerably fast until DA becomes stationary concentration, that is,

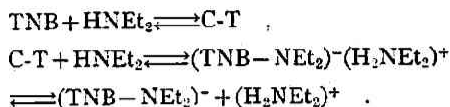


where A represents acetone. Even with variable concentrations of $[\text{DEA}]_0$ ($10^{-2} \sim 2 \times 10^{-2}$ mole/l), if $[\text{TNB}]_0$ kept constant (2×10^{-5} mole/l), optical densities at $520 \text{ m}\mu$ after long time are constant. On the other hand, at constant $[\text{DEA}]_0$ ($\sim 10^{-2}$ mole/l), optical density is proportional to $[\text{TNB}]_0$. These results indicate the absence of the reverse reaction of step (5).

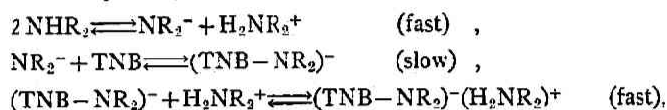
Fast reaction

The complex, C, initially formed, is not identical with the C-T complex (I), as mentioned above. The formation of an ion pair of Meisenheimer type, (II) $(\text{H}_2\text{NR})^+$, from TNB and piperidine was re-

ported in acetonitrile⁶⁾. Liptay *et al.*, suggested the scheme²²⁾,

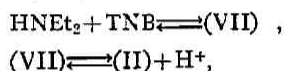


In this scheme, however, the rate of formation of $(\text{TNB}-\text{NEt}_2)^-$ must be of second order in DEA. But if the following scheme is accepted^{7b)},



the rate is of first order with respect to DEA.

Furthermore, if a zwitterion complex as (VII) is formed^{7a)}, the following steps may be accepted,



but these processes can not be distinguished.

Although the authors could not give no conclusive evidence from the kinetic study, the intermediate complex, C, may be either one of Meisenheimer type, (II), or a zwitterion of (VII).

Anyway, within a short reaction time when the contribution of the following secondary reaction can be negligible, only the step (3) may be considered,

$$\frac{d[\text{C}]}{dt} = k_f[\text{TNB}][\text{DEA}] - k_b[\text{C}] \quad (6)$$

Under the experimental condition, $[\text{TNB}]_0 \ll [\text{DEA}]_0$, $[\text{DEA}]$ may be regarded as nearly equal to $[\text{DEA}]_0$ during the reaction. Denoting the equilibrium concentration of C by $[\text{C}]_0$ in the step (3), the integration of equation (6) reduces to,

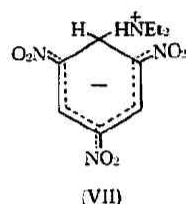
$$\ln \frac{[\text{C}]_0 - [\text{C}]}{[\text{C}]_0 - [\text{C}]_0} = -(k_f[\text{DEA}]_0 + k_b)t \quad (7)$$

Representing optical density at $472 \text{ m}\mu$ by D and assuming Beer's law is obeyed,

$$\ln \frac{D_e - D}{D_e - D_0} = -(k_f[\text{DEA}]_0 + k_b)t \quad (8)$$

hence the plot of Guggenheim's method is able to be adopted and its slope gives the relation (1).

The kinetic and thermodynamic parameters listed on Table 1 are quite different from Caldin's⁴⁾. The remarkable contrast is that ΔH° obtained by Caldin is negative ($-0.2 \pm 1.5 \text{ kcal/mole}$), while, in the present study ΔH° is positive (3.5 kcal/mole), although the direct comparison is impossible because of different kinetic order. The apparent activation energy, in general, is dependent on temperature²³⁾, so the value of ΔH° derived from the activation energies is variable with temperature and it is not so surprising that it varies by $2 \sim 3 \text{ kcal/mole}$ due to the temperature difference of 100°C . But the difference of reaction order and the change from exothermic reaction to endothermic one with temperature,



22) W. Liptay and N. Tamberg, *Z. Elektrochem.*, **66**, 59 (1962)

23) A. Frost and R.G. Pearson, "Kinetics and Mechanism", p. p. 24, 94, John Wiley & Sons, Inc., New York, London (1962)

including the solvent effects, are unsolved problems.

Considering that ΔH° and ΔS° are both positive and that ΔS_f° and ΔS_b° are both negative, it can be concluded that the transition state is remarkably solvated and significant desolvation accompanies the complex formation.

Slow reaction

Although Foster elucidated the step $\text{II} \rightarrow \text{IV} + \text{V}^8$, it is doubtful how important the reaction is in such a dilute solution as in the present study.

The product (VI) having a maximum peak at $520\text{m}\mu^8$ is not identified, but considering the time dependence of the variation of optical density and the spectra in Fig. 2, it seems reasonable to conclude that (VI) is mainly produced in a dilute solution and that the contribution of (II) and (III) to optical density at $516\text{m}\mu$ is negligible. The product, P, in the step (5) may be identical with (VI), although the product will be formed not through the Foster's postulate but through the steps, (3), (4) and (5), which well explain the results that the development of the product is quite characteristic of the consecutive reactions.

From equation (5), the rate of appearance of P can be represented by equation (9),

$$\frac{d[P]}{dt} = k_4[C][DA], \quad (9)$$

assuming that reaction (4) is slow and DA is in steady-state, this equation is reduced to,

$$\frac{d[P]}{dt} = k_3[DEA] = k_3[DEA]_0. \quad (10)$$

So the slopes in Fig. 7 correspond to k_3 and the following numerical values are obtained.

$$\left. \begin{aligned} k_3 \text{ (at } 25^\circ\text{C)} &= 2.0 \times 10^{-6} \text{ (sec}^{-1}\text{)} , \\ k_3 \text{ (at } 30^\circ\text{C)} &= 2.4 \times 10^{-6} \text{ (sec}^{-1}\text{)} . \end{aligned} \right\} \quad (11)$$

The value of k_4 also can be estimated from the relationship between the initial rate of the development of optical density at $516\text{m}\mu$ and aging time. When extrapolated $t \rightarrow 0$ in Fig. 6, C can be considered to be in equilibrium concentration, $[C]_0'$. As k_3 was obtained, the concentration of DA formed during the aging, $[DA]_0'$, can be determined. The concentration of DEA after the aging time, Δt , being denoted by $[DEA]_0'$, the following equation can be derived,

$$[DEA]_0' = [DEA]_0 \exp(-k_3 \Delta t), \quad (12)$$

$$[DA]_0' = [DEA]_0 \{1 - \exp(-k_3 \Delta t)\}. \quad (13)$$

Moreover, the equilibrium constant is given by

$$\frac{[C]_0'}{([TNB]_0 - [C]_0')[DEA]_0'} = K. \quad (14)$$

and using equation (12),

$$[C]_0' = \frac{K[DEA]_0[TNB]_0 \exp(-k_3 \Delta t)}{1 + K[DEA]_0 \exp(-k_3 \Delta t)}. \quad (15)$$

Now, the initial slope in Fig. 6 is represented by the following,

$$\left(\frac{d[P]}{dt} \right)_{t \rightarrow 0} = k_4[C]_0'[DA]_0'. \quad (16)$$

Substituting equations (13) and (15) into equation (16), the following equation (17) is derived.

$$\left(\frac{d[P]}{dt}\right)_{t \rightarrow 0} = k_4 \left[\frac{K_4 [\text{TNB}]_0 [\text{DEA}]_0^2 \{ \exp(-k_3 \Delta t) - \exp(-2k_3 \Delta t) \}}{1 + K [\text{DEA}]_0 \exp(-k_3 \Delta t)} \right] \quad (17)$$

The term in the bracket [] of the right hand side of equation (17), which is denoted as X^* , can be

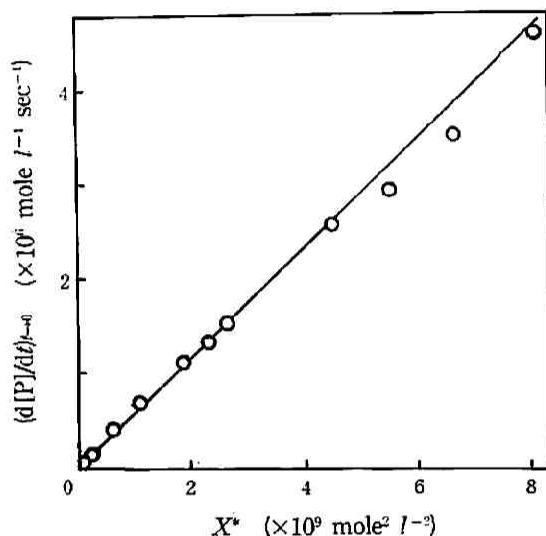


Fig. 8 The variation of initial reaction velocity measured at 516 m μ at 25°C

calculated for the arbitrary aging time, the plot of $(d[P]/dt)_{t \rightarrow 0}$ against X^* , giving a straight line as illustrated in Fig. 8, and the numerical value of k_4 was obtained,

$$k_4 (\text{at } 25^\circ\text{C}) = 5.6 \times 10^2 \text{ l/mole-sec.}$$

Although the conformation of the product could not be elucidated, the experimental results may be explained by the reaction scheme, (3), (4) and (5).

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